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Insights from a Theoretical Approach on the Weak Intermolecular Forces: the Transition from Van Der Waals to Chemical Bond

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Summary

Understanding the nature of weak chemical interactions is a long-standing, fundamentally important endeavour in chemistry, since such interactions are known to control reaction stereodynamics in the gas phase and on surfaces, and play a crucial role in biological and supramolecular systems, with repercussions in many fields, such as crystal engineering, molecular recognition, drug design and catalysis. A detailed characterization of these non-covalent interactions is not trivial and only a theoretical support can shed the light on the characterization of the leading components that, balancing each other, define the strength of the interactions. The main components for weak interactions are, basically, electrostatic, induction, dispersion, Pauli repulsion and charge transfer: their deep knowledge and modelling are crucial to obtain information about the whole interaction as well as to establish the peculiar effect of each term. In order to adequately describe weak chemical interactions, high level quantum mechanics calculations are necessary

This thesis is the result of an international joint supervision PhD with the Vrije Universiteit Amsterdam, under the supervision of Prof. Dr Matthias Bickelhaupt and Prof. Dr Cèlia Fonseca-Guerra. It has the important goal to underline the essential role of the computational investigations in the field of non-covalent interactions. Our analysis builds on a quantitative estimation of each component that makes up the intermolecular interactions, using computational tools and, where is possible, an analytical approach to model them. Furthermore, our investigations have been also supported by the molecular-beam scattering experiments performed by Prof. Fernando Pirani at University of Perugia, in order to recover a quantitative knowledge of the balancing components of the investigated weak interaction.

In the proceedings of the thesis, challenging investigations has been performed in order to obtain insights from particular compounds not experimentally isolated yet, such as some noble gas adducts. The *Charge-Displacement function (CDF)* has been largely used in order to estimate the charge displaced upon the formation of the adduct, especially in hydrogen and halogen bonds interactions. Furthermore, biological systems have been investigated in order to verify the performances of tools, tuned on small prototypical models, on larger systems.

The outline of the thesis is as follow. In Chapter 1 we studied the puzzling stability and short distances predicted by theory for helium adducts with some highly polar molecules: for the first time we have unambiguously ascertained that helium is able not only to donate electron density, but also,

unexpectedly, to accept electron density in the formation of weakly bound adducts with highly polar substrates. In Chapter 2, the nature of the interaction of the weakly bound Be-He has been investigated, using an integrated theoretical approach together with the development of a semi-empirical formulation of the interaction potential: the analysis has shown that the excited state Be(1D) is involved and that the leading interaction component is the charge transfer. The Chapters 3 and 4 are entirely dedicated to the investigation of the halogen bond in both small prototypical model systems and larger bioorganic systems. Indeed, in Chapter 3, we reported the results of an integrated approach by means of high-level *ab initio* computations and molecular-beam scattering experiments for the investigation of the potential energy surfaces of the series of noble-gas—Cl₂ adducts. The results have permitted to characterize the interaction, both in the ground and excited states. In Chapter 4 the role of the halogen bond in a series of *peri*-substituted naphthalenes mimicking the catalytic function of deiodinase enzymes has been computationally examined, revealing the crucial role of the formation of this weak interaction in the rate-determining step of the whole enzymatic process. The Chapter 5 is dedicated to the interplay between halogen and hydrogen bond in the stabilization of water adducts with apolar molecules: by an experimental-computational approach, the role of various components has been identified in order to formulate a model of interaction potential. In Chapter 6 the cooperativity of the hydrogen bond in supramolecular systems has been explored: the source of the synergy has been investigated, revealing that the origin is both electrostatic and orbitalic; in particular we have shed the light on the reason why there is an enhancement of the aromaticity when the investigated polymeric chains are made up by aromatic monomers.